

Historic, Archive Document

Do not assume content reflects current scientific knowledge, policies, or practices.

United States Department of Agriculture,

BUREAU OF CHEMISTRY—Circular No. 20.

H. W. WILEY, Chief.

EXTRACTS FROM THE PROCEEDINGS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1904.

[An advance circular, giving the recommendations of referees as adopted, motions, and appointments affecting the work of 1905.]

REPORTS OF COMMITTEES ON RECOMMENDATIONS OF REFEREES.

COMMITTEE A.—C. B. WILLIAMS, CHAIRMAN.

(Phosphoric acid, potash, nitrogen, soils, ash, and insecticides.)

-(1) SOILS.

It is recommended—

1. That the investigation of methods for the determination of water-soluble plant food in soils be continued.

Adopted.

2. That methods for determining the easily soluble plant food be further investigated by using acid solutions of greater strength than N/200, as was recommended by the referee last year and briefly reported on by Professor Peter in the referee's report.

Adopted.

3. That this association encourage the reporting of soil analyses, so far as practicable, upon the uniform basis of chemical elements.

A discussion on this recommendation brought out the fact that while uniformity in reporting all analytical results was greatly to be desired, it was not deemed advisable, and would bring no relief to adopt such a measure unless it were concurred in by others. Mr. Wheeler emphasizing the point that the comparison of results obtained by the association with those reported by other chemists, especially Europeans, must be considered. The discussion resulted in the following resolution offered by Mr. Davidson:

"*Resolved*, That a committee of five be appointed to consider the whole question of unifying the terms in which analytical results are reported and report to the association at its next meeting."

Adopted.

(2) ASH.

It is recommended—

1. That the study of the nitric-acid and peroxid methods be continued next year.

Adopted.

2. That the referee on ash for next year be requested to make determinations of the total sulphur in the samples used for cooperative work by the Barlow-Tollens, or "absolute," method for sulphur in organic combinations.

Adopted.

(3) NITROGEN.

It is recommended—

1. That the alkaline permanganate method, amended to read as stated below, be adopted as a provisional method.

ALKALINE PERMANGATE METHOD.

Weigh out an amount of samples containing 0.045 gram of organic nitrogen and transfer to a 600 cc distillation flask. After connecting with condenser to which the receiver containing standard acid has been attached, digest with 10 cc of alkaline permanganate solution (16 grams of KMnO_4 and 150 grams of sodium hydrate, dissolved in water and made to bulk of 1 liter) for thirty minutes below the boiling point. Then boil until 85 cc of distillate is obtained. If the material shows a tendency to adhere to the sides of the flask an occasional gentle rotation is necessary during distillation.

After some discussion as to whether 100 cc of the alkaline permanganate solution was sufficient the recommendation was adopted.

2. That the study of availability by both neutral and alkaline methods be continued, particularly with a view of determining the amount of material to be used in the neutral method on commercial fertilizers.

Adopted.

(4) INSECTICIDES.

It is recommended—

1. That Methods I and IV of the four modifications of the Avery-Beans method of determining total arsenic in Paris green be adopted as optional official methods.

It being the first year that the adoption of these methods as official had been recommended they were referred to the association for final action in 1905, in accordance with the established precedent in changing or making additions to official methods.

2. That in titration of arsenic N/20 instead of N/10 iodine be used, as Mr. Davidson suggests.

Adopted.

3. That the electrolytic method be adopted as the official method of determining copper in Paris green and copper carbonate, and that the thiosulphate method be adopted as an optional method, using N/20 instead of N/10 thiosulphate solution.

Finally adopted through the words "copper carbonate" having been brought before the association in 1903, and the remainder of the recommendation referred to the association for final action in 1905.

4. That the work on London purple be continued.

Adopted.

5. That the volumetric silver nitrate method be adopted as the official method of determining cyanogen in potassium cyanid, and that N/20 instead of N/10 solution of silver nitrate be used.

Finally adopted, having been before the association in 1903.

6. That the methods of examination of soda lye be further tested.

Adopted.

7. That the Kissling method of determining nicotin be adopted as the official method, and that Mr. Emory's polariscopic method be further tested.

Finally adopted, having been before the association in 1903.

8. That the hydrogen peroxid method, suggested by Mr. Avery, for determining sulphur in sulphur dips and similar compounds be adopted as a provisional method and tested by the association next year.

Adopted.

9. That the Blank and Finkenbiener peroxid method be adopted as the official method of determining formaldehyde in strong solutions, and that the Romjyn potassium cyanid method be adopted as an official method for analyzing dilute solutions.

Recommended for the first time, and action accordingly deferred until the meeting of 1905.

10. That methods of comparing chlorid of lime be compared.

Adopted.

11. That attention be given to the analysis of crude oil in disinfectants.

Adopted.

(5) POTASH.

It is recommended—

1. That the directions for making the solution in mixed fertilizers given under the determination of potash in Bulletin 46, page 21, be made to read as follows:

Boil 10 grams of the sample with 300 cc of water plus 5 cc of hydrochloric acid for thirty minutes. Add a few drops of phenolphthalein and carefully neutralize with sodium hydrate free from potash, avoiding a large excess. Add sufficient powdered ammonium oxalate to precipitate all the lime present, cool, dilute to 500 cc, mix, and pass through a dry filter.

The method for the solution of potash salts is to remain as it is.

2. That the directions for the determination of moisture in potash salts, sodium nitrate, and sulphate of ammonia, given under the determination of moisture, Bulletin 46, page 11, be made to read as follows:

In potash salts, sodium nitrate, and ammonium sulphate heat 2 grams at 130° in oil oven for 10 hours. The loss in weight is considered as moisture.

As both of these recommendations involved changes in official methods, action on them was deferred until 1905.

(6) PHOSPHORIC ACID.

1. That the referee for next year plan field and pot experiments with cultivated plants, looking toward the establishing of the relative value of the total phosphoric acid content of basic phosphate slags (both foreign and domestic), redonda and precipitated phosphates, of different degrees of fineness, in comparison with the phosphoric acid contained in acid phosphate and other common phosphatic materials found on sale in our markets, and invite cooperation on as many soil types and by as many workers as possible.

Adopted.

2. That further study be made on the methods for determining total and available lime contained in basic phosphatic slags.

After some discussion this recommendation was referred to the referee for 1905, with authority to act at his own discretion.

3. That a study of the methods for determining total phosphoric acid in basic phosphatic slags be continued.

Adopted.

4. That the referee for next year make a study of the solubility of the phosphoric acid in samples of the same slag of different degrees of fineness.

Referred to the referee for 1905, with authority to act at his own discretion.

COMMITTEE B.—C. A. BROWNE, JR., CHAIRMAN.

(Dairy products, foods and feeding stuffs, sugar, and tannin.)

(1) SUGAR.

1. Chemical Methods.

(a) That the referee on chemical methods devote as much time during the coming year as seems desirable, in cooperation with the Committee of the International Commission for Unifying Methods of Sugar Analysis having in charge the revision of reducing-sugar methods, for the purpose of obtaining more satisfactory and more uniform methods of determining reducing sugars.

Adopted.

2. Special Analytical Methods.

(a) That the methods for the determination of levulose and dextrose in the presence of sucrose be given further trial.

(b) That the study of methods for the identification and analysis of the vegetable gums be continued, and

(c) That some effort be made toward perfecting methods for the determination of caramel and the other organic solids which accompany sugar in cane and beet products.

Adopted.

3. Molasses Analysis.

(a) That the association consider the adoption of the neutral oxalate of potassium in place of sodium carbonate as a precipitant for lead from clarified sugar solutions which are to be tested for reducing sugars. It has been known for several years that an excess of sodium carbonate redissolves a portion of the lead precipitate in the presence of invert sugar. It has been found by the associate referee that potassium oxalate does not behave in this objectionable manner, and, so far as he has been able to ascertain, there is no drawback to its use.

It is not recommended that the present method be changed this year, but it is suggested that the referee on sugar for the next year be requested to test this new precipitant.

Referred to the referee for 1905, with instructions to act at his own discretion.

(b) That the referee on sugar, or one of his associates, be requested to submit to collaborative test next year the methods of molasses analysis outlined at the meeting in 1903 (Bulletin 81, p. 175).

Adopted.

(2) TANNIN.

It is recommended—

1. That further research be made with the object of establishing a limit of temperature at which the determination of soluble solids and insolubles shall be conducted.

Adopted.

2. That the method for analysis of barks, woods, etc., as set forth in the referee's report be printed as a provisional method, and trials continued until it has been perfected.

Adopted.

This method is as follows:

PROVISIONAL METHOD FOR BARKS, WOODS, LEAVES, ETC.

I. *Moisture determination.*

Immediately upon receipt of sample grind or crush as finely as possible 25 grams, and dry for 12 hours at 100° C., reweigh, and calculate difference as H₂O.

II. Preparation of sample for extraction.

Barks, woods, leaves, and other tanning materials, such as nut galls, myrobalsams, etc., should be dried sufficiently to facilitate grinding and then ground to such a degree of fineness that the sample will pass through a sieve of 14 meshes to the inch (linear).

In case of a coarser residue being left after sieving the portion ground, it should be reground until the entire quantity passes through the sieve. A style of grinder should be used that will make a granular preparation of the desired size, not finer. An excess of dust and very fine particles must be guarded against in order that a rapid and complete extraction be obtained.

III. Quantity of sample to be used for extraction.

Such a quantity of the material to be analyzed should be taken as will yield a sufficient volume of liquor having a specific gravity of 1.0025 at 15° C. Should the gravity of the liquor prove greater than the above, dilute to the desired point with water about 80° C. If, however, it should prove impracticable to obtain from spent material the necessary volume of liquor of the gravity specified, the gravity should be taken and the quantity of hide powder used to precipitate the tannin, reduced in proportion.

IV. Extraction of sample.

The extraction may be carried out in any form of extractor that will give complete extraction, with a yield of not more than 1 liter of liquor. A temperature of 100° C. should be maintained throughout the entire operation, except in the case of sumac and starch-bearing materials, when a maximum of 80° C. will be found better, and extraction continued until resulting liquor shows no precipitation with gelatin solution, as by the method for testing nontannins. Should the volume of liquor prove insufficient, dilution should be made immediately with water at 80° C. to as near the mark as possible.

In case of pulverized or finely ground material, such as sumac, powdered nut galls, etc., the extraction will be materially assisted by thoroughly mixing the sample with glass sand free from iron and matter precipitable or soluble in hot tannin solution.

V. Total solids.

After extraction and final dilution cool slowly to about 20° C., shake thoroughly, allow to stand for one hour, then pipette 100 cc into a tared dish, evaporate, dry, and weigh according to method in Bulletin 46.

VI. Soluble solids, nontannins and tannin.

The determination of the above items should be conducted as by the method in Bulletin 46.

NOTES.—In all cases it is best to conduct the analyses from a dry basis—that is, with the material dried at 100° C. If the analysis is made to determine the tanning or commercial value, results should be calculated back to the natural condition of the material. In the case of analyses made for comparison between fresh and spent materials, and in controlling tannery or extract manufacturing processes, results are more conveniently calculated and recorded on a dry basis.

Attention must be given to the quantity of hide powder used in determining nontannins. See Paragraph III, Quantity of Sample, etc., above.

3. That the method for the determination of acid in tannin solutions, with the alternative of using the cold charcoal method, be continued as a provisional method and given further study.

Adopted.

4. That the referee for 1905 make a study of present methods of analysis of tannery-yard liquors, especially spent or "sapped" liquors.

Adopted.

5. That the recommendations submitted in the report for 1903 be embodied in the official (?) method.

These changes read as follows:

1. That the last sentence of Paragraph II, Quantity of Material (Bul. 46, Methods of Analysis, p. 79), be changed to read as follows:

In the case of extracts, weigh in a weighing bottle fitted with a ground-glass stopper such quantity, etc.

2. That the last sentence of Paragraph V, Soluble Solids (Bul. 46, Methods of Analysis, p. 80), be changed to read as follows:

That the funnel shall be covered with a plate during filtration, and all other means be taken to guard against evaporation.

Discussion followed as to whether the methods on tannin, as given in Bulletin No. 46, were official or not, and the secretary was empowered to determine this point and adopt these changes, officially or provisionally, in accordance with the facts. By reference to Bulletin No. 73, Proceedings of the Nineteenth Annual Convention, footnotes on pages 174 and 175, it will be seen that the same question was raised and subsequent investigation showed that the tannin methods *had never been adopted as official*. A circular letter addressed to the executive committee procured permission to insert the word "provisional" over the methods on tannin in Bulletin No. 46 when revised.

Accordingly the above recommendations are adopted as changes in the provisional method appearing in Bulletin No. 46.

(3) FOODS AND FEEDING STUFFS.

As no work was done on this subject in 1904, the recommendations for the preceding year were again referred to the referee for 1905.

It is recommended—

1. That the referee be requested to study the composition of the ether extract obtained after digesting with pepsin the residue obtained by the official method of fat extraction.

2. That the modified König method for the determination of crude fiber be further investigated, especially to ascertain whether the glycerol-acid mixture hydrolyzes any of the true fiber.

(4) DAIRY PRODUCTS.

It is recommended—

1. That the two lines of work of this year be continued for another year, i. e., effect of preservatives on the albumin of milk and methods for detecting renovated butters.

2. That the referee be requested to study the methods for determining sugars in condensed milk and milk powders, or dried milks.

Adopted.

COMMITTEE C.—W. D. BIGELOW, CHAIRMAN.

(1) BAKING POWDER AND BAKING CHEMICALS.

It is recommended—

That the Wolff method for the detection of tartaric acid and tartrates and the silver mirror test, after shaking sample with 10 per cent ammonia water and filtering (see Brooks on "The Rapid Analysis of Cream of Tartar and Tartaric Acid Baking Powders," J. Amer. Chem. Soc., 1904, 26: 813), be further studied.

Adopted.

(2) TEA AND COFFEE.

It is recommended—

That the methods outlined by the referee on tea and coffee be adopted provisionally.

Adopted.

These methods are as follows:

TEA.

1. Detection of stems, dust, and foreign leaves.

Place 1 gram of tea in a 300 cc casserole, add 200 cc of water and boil for 15 minutes. This treatment will cause the leaves to unroll and a megascopic examination will reveal the presence or absence of stems or dust, while the leaves will be in condition for examination as to their form and structure.

2. Detection of facing.

Tea is faced by treating with mineral pigments, graphite, catechu, etc. Mineral pigments can be detected in the ash, or the tea may be shaken up with a large volume of water, and the water separated from the leaves by a sieve, when the insoluble mineral substances used in facing will settle, and can be removed by filtration for further examination, the catechu and other soluble substances being in the filtrate.

3. Chemical analysis.

The sample should be ground fine enough to pass through a 40-mesh sieve. Determine the moisture, ash, soluble ash, sand, alkalinity of the ash, phosphates, petroleum ether extract, crude fiber, and nitrogen as described under coffee.

4. Water extract.

Method of Krauch.^a—Treat 20 grams of tea with 400 cc of water and heat on a boiling water bath for six hours. Filter through a tared filter, wash with water until the filtrate measures 1,000 cc, dry and weigh the residue. The water-soluble substance is determined by difference.

5. Volatile oil.

Distill 100 grams of tea with 800 cc of water, extract the filtrate several times with petroleum ether, evaporate the combined petroleum ether extracts at the room temperature, dry in a desiccator and weigh.

6. Determination of theine.

Method of P. Dvorkowitsch.^b—Digest 10 grams of the powered tea with 200 cc of boiling water for five minutes, and decant the solution; repeat the treatment twice and boil the residue twice with 200 cc of water. Make up the combined solutions of 100 cc and extract a portion with petroleum ether to remove the fat, etc. To 600 cc of the fat-free solution (equivalent to 6 grams of tea) add 100 cc of 4 per cent barium hydroxid, mix and filter. To 583 cc of the filtrate (equivalent to 5 grams of tea) add 100 cc of a 20 per cent solution of sodium chlorid, and extract three times with chloroform. Distill the majority of the chloroform from the combined extracts, place the residue in a tared dish, evaporate the remainder of the chloroform, dry at 100° and weigh. The theine is usually of sufficient purity to render a nitrogen determination unnecessary.

*7. Determination of tannin.**Procter's Modification of Löwenthal's Method.*^c

Reagents: (1) Potassium permanganate solution containing about 1.33 grams per liter.

(2) Tenth normal oxalic acid solution (6.3 grams per liter).

(3) Indigo carmine solution, containing 6 grams indigo carmine (free from indigo blue) and 50 cc concentrated sulphuric acid per liter.

(4) Gelatin solution, prepared by soaking 25 grams of gelatin for one hour in a saturated sodium chlorid solution, heating until the gelatin is dissolved, and making up to 1 liter after cooling.

^a König. Zts. Nahr. Genussm., 3d edition, p. 1057.

^b Ibid., 4th edition, p. 1010.

^c U. S. Dept. of Agr., Division of Chemistry, Bul. 13, Part 7, p. 890.

(5) Mixture of 975 cc saturated sodium chlorid solution and 25 cc concentrated sulphuric acid.

(6) Powdered kaolin.

Obtain the value of the potassium permanganate in terms of the oxalic acid.

Boil 5 grams of the tea for half an hour with 400 cc of water; cool, transfer to a graduated 500 cc flask and make up to the mark. To 10 cc of the infusion (filtered if not clear) add 25 cc of the indigo carmine solution and about 750 cc of water. Then add from a burette the potassium permanganate solution, a little at a time while stirring, till the color becomes light green, then cautiously, drop by drop, until the color changes to bright yellow or further to a faint pink at the rim. The number of cubic centimeters of permanganate used furnishes the value a of the formula.

Mix 100 cc of the clear infusion of tea with 50 cc of gelatin solution, 100 cc of salt acid solution, and 10 grams of kaolin, and shake several minutes in a corked flask. After settling, decant first the clear supernatant liquid through a filter and finally bring the precipitate upon the filter. Mix 25 cc of the filtrate (corresponding to 10 cc of the original infusion) with 25 cc of the indigo solution and about 750 cc of water, and titrate with permanganate as before. The number of cubic centimeters of permanganate used gives the value b , $a-b=c$, c =permanganate required to oxidize the tannin. Assume that 0.04157 gram tannin (gallotannic acid) is equivalent to 0.063 gram oxalic acid.

COFFEE.

A. Raw Coffee.

Raw coffee is sometimes treated with water to increase its weight. This form of adulteration can be detected by drying 5 grams of the ground coffee at 100° for three hours. The amount of moisture in raw coffee is from 9 to 13 per cent.

The inferior grades are sometimes colored to imitate the better grades. Such pigments as ochre, litharge, lead chromate, and chromic oxid, such organic colors as indigo, turmeric, azo yellow, malachite green, methyl green, etc., have been used for this purpose. The mineral colors can be identified in the ash or removed from the bean by shaking with water, in which case the soluble colors can be identified in the solution and the insoluble ones in the residue.

B. Roasted Coffee.

1. EXAMINATION OF THE WHOLE BEANS.

Examine the sample megascopically in order to detect foreign substances. Artificial coffee beans are apparent from their exact regularity of form; coffee pellets are made from roasted wheat mash and are of a brown color, possessing a very characteristic ellipsoidal form; roasted legumes and lumps of chicory are sometimes present and are easily identified by the practiced eye. Coffee is glazed by treating the raw beans with molasses, sugar solution, glycerin, or fats and waxes, and then roasting.

2. DETECTION OF SUGAR GLAZING.

Method of Stutzer & Reitnair.^a—Twenty grams of the whole beans are treated with 500 cc of water in a liter flask and shaken vigorously for five minutes. Complete the volume to the mark with water, mix, filter and determine the solids and ash in 50 cc of the filtrate. The difference between these two figures gives the soluble organic matter, which, in unglazed coffee, is from 0.44 to 0.72 per cent, and in glazed coffee from 1.81 to 8.18 per cent.

3. DETECTION OF GLYCERIN.

Proceed as directed under wines ^b on a portion of the filtrate from 2.

4. DETECTION OF FATS AND WAXES.

Method of E. Spath.^c—Treat 100 to 200 grams of the beans with low boiling petroleum ether for ten minutes, pour off the petroleum, and repeat the process.

^a Pharm. Centralhalle, 22: 134.

^b U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 82.

^c Forschungsberichte über Lebensmittel, 1895, 2: 223.

Filter the combined petroleum ether extracts, evaporate the solvent, and determine the saponification number and index of refraction of the residue.

C. *Physical Examination of Commercial Ground Coffee.*

5. MEGASCOPIC EXAMINATION.

The practiced analyst can tell at a glance if there is any appreciable amount of adulteration. Roasted grains possess a glossy appearance entirely foreign to that of roasted coffee, and if roasted legumes are present, fragments of the hulls can be seen.

6. MICROSCOPIC EXAMINATION.

Grind a portion of the sample in a porcelain mortar to the requisite degree of fineness, which one soon learns by experience, place a portion on a microscope slide, add a drop of water, place a cover glass on the specimen, and rub out between the thumb and finger. Too much rubbing or grinding is to be avoided, as the characteristic microscopical appearance of the cell structure of the coffee will be destroyed. Examine with a $\frac{1}{4}$ -inch objective and a 1-inch ocular.

With pure coffee one sees fragments of the hexagonal cells and the oil drops. Roasted grains are apparent from the starch grains which, though somewhat distorted by the roasting, can be easily identified. Roasted legumes show the starch granules, and in a striking manner, the hulls resembling bunches of matches. When roasted chicory is present the cellular tissue is apparent and also fragments of the juice ducts. For photomicrographs of these substances see the Massachusetts State Board of Health, Annual Report for 1900, Plate VI, Figs. 21, 22, 23, 24, Leach. "Food Inspection and Analysis." John Wiley & Sons. Plate XIV, Figs. 173, 174, 175, 176; Plate XV, Figs. 177, 178, 179, 180; Plate XVI, Figs. 181, 182, 183.

D. *Chemical Examination of Coffee.*

7. PREPARATION OF THE SAMPLE.

Grind until the sample will pass through a forty-mesh sieve.

8. MOISTURE.

Place 5 grams of the sample in a flat bottomed platinum dish and dry for three hours in an oven at 100°, cool in a desiccator, and weigh. The loss is moisture.

9. TOTAL ASH.

Burn the dry residue from the above treatment in a muffle, cool, and weigh.

10. WATER SOLUBLE ASH.

Boil the ash as obtained above in 50 cc of water, filter through an ashless filter, wash with boiling water, place the filter in the platinum dish, ignite, and weigh. The difference between this weight and that of the total ash gives the weight of the soluble ash.

11. ASH INSOLUBLE IN ACID OR SAND.

Boil the ash insoluble in water with 50 cc of 10 per cent hydrochloric acid, filter on an ashless filter paper, wash with water, ignite, and weigh.

12. CHLORIN.

Treat the water solution of the ash (filtrate of 10) with an excess of dilute sulphuric acid, add a slight excess of magnesia and titrate with tenth normal silver nitrate, using potassium chromate as an indicator. (This determination is useful if chicory be present, and also to determine if sea water has been used as a make-weight in raw coffee.)

13. ALKALINITY OF THE ASH.

Weigh 10 grams of the coffee in a platinum dish and burn to an ash in a muffle, boil the ash with 100 cc of water for ten minutes, filter, and wash with

water until free from alkali. To the filtrate add from a burette an excess of tenth normal hydrochloric acid, boil to expel the carbonic acid, and determine the excess of acid by titrating with tenth normal alkali, using phenolphthalein as an indicator, express results as cubic centimeters of tenth normal acid required to neutralize the ash of one gram of coffee and also one gram of coffee ash.

14. SOLUBLE PHOSPHATES.

Make the final solution of 13 slightly acid with dilute hydrochloric acid and evaporate to dryness, add 50 cc of boiling water and titrate in the usual manner with uranium solution.^a

15. INSOLUBLE PHOSPHATES.

Dissolve the insoluble ash of 13 in dilute hydrochloric acid, evaporate to dryness, add ten drops of dilute hydrochloric acid to the residue, dissolve in 50 cc of boiling water, add 1 gram of sodium acetate, and titrate with uranium solution.

16. PETROLEUM-ETHER EXTRACT.

Dry 2 grams of coffee at 100°, extract with petroleum ether (boiling points from 35° to 50°) for 16 hours, evaporate the solvent, dry the residue at 100° and weigh.

17. TOTAL NITROGEN.

Use the regular Gunning method, taking three grams of the sample. This gives the total nitrogen due to both the proteids and the caffeine. To obtain the proteid nitrogen, subtract from the total nitrogen the nitrogen due to caffeine obtained by direct determination on the separated caffeine or by calculation (caffeine $\div$ 3.464 = nitrogen).

18. COLD WATER EXTRACT.

Winton's Method.—Place 4 grams of the sample in a 200 cc flask, add water to the mark, and allow to macerate 8 hours with occasional shaking; let stand 16 hours more without shaking, filter, evaporate 50 cc of the filtrate to dryness in a flat-bottomed dish, dry at 100° and weigh.

19. REDUCING SUGARS.

Treat 100 cc of the cold water extract obtained in 18 with 0.5 gram of lead acetate, shake until dissolved, add 1 gram of sodium sulphate, shake until dissolved, filter, and determine the reducing sugars in the filtrate. Calculate as dextrose.

20. CANE SUGAR.

Take one-half the normal weight for the Schmidt & Haensch polariscope (13.024 grams), place in a 100 cc flask, add water, mix, add 5 cc of lead subacetate, make up to the mark, mix well, and filter. Treat another half normal weight in the same manner in a 200 cc flask. Polarize the two solutions in the 200 mm tube. Invert the two solutions and polarize as usual. The product of the two direct readings divided by their difference,^b and the quotient multiplied by 2 gives the true direct reading. Obtain the true invert reading in a similar manner and calculate the sucrose by Clerget's formula. (So-called soluble coffee has been found containing as high as 30 per cent of cane sugar.)

21. COPPER-REDUCING MATTER BY ACID CONVERSION.^c

Use 4 grams of the sample and apply the official method.

22. COPPER-REDUCING MATTER BY DIASTASE.^d

Use 4 grams of the sample and apply the official method.

^a Sutton's Volumetric Analysis, 8th ed., p. 313.

^b Double Solution Method of Wiley and Ewell, Analyst, 21: 182.

^c Bul. 46, p. 25, section (c).

^d Ibid., section (d).

23. CRUDE FIBER.^a

Use the official method, taking the residue exhausted by the petroleum ether for the sample.

24. TEN PER CENT EXTRACT.

Method of McGill.^b—Weigh into a tared flask the equivalent of 10 grams of the dried substance, add water until the contents of the flask weigh 110 grams, connect with a reflux condenser and heat, beginning the boiling in from 10 to 15 minutes. Boil for 1 hour, cool 15 minutes, weigh again, making up any loss by the addition of water, filter, and take the specific gravity of the filtrate at 15°.

According to McGill, a 10 per cent extract of pure coffee has a specific gravity of 1.00986 at 15°, and under the same treatment chicory gives an extract with a specific gravity of 1.02821. In mixtures of coffee and chicory the approximate percentage of chicory may be calculated by the following formula:

$$\text{Per cent of chicory} = 100 - \frac{(1.02821 - \text{sp. gr.}) 100}{0.01835}$$

The index of refraction of the above solution may be taken with the Zeiss immersion refractometer or with the Abbé refractometer.

A 10 per cent coffee extract $n_D 20^\circ = 1.3377$.

A 10 per cent chicory extract $n_D 20^\circ = 1.3448$.

Determinations of the solids, ash, sugar, nitrogen, etc., may be made on the 10 per cent extract, if desired.

25. CAFFEINE.

Method of Hilger and Fricke.^c—Take 5 to 10 grams of coffee, add 100 cc of water and boil, filter, and treat the residue twice more with boiling water. Add to the united filtrates an excess of lead acetate, filter and wash. Treat the filtrate with hydrogen sulphid to remove the excess of lead, filter, wash, and evaporate the filtrate to dryness in a Hoffmeister schälchen with some sand and a little magnesia. Crush the schälchen between filter paper, place in a continuous-extraction apparatus, and extract with chloroform until exhausted. Dry the chloroform extract at 100° and weigh as caffeine. If the caffeine does not appear to be pure, determine the nitrogen in the residue by the Gunning method. $N \times 3.464 = \text{caffeine}$.

26. CAFFETANNIC ACID.

Krug's Method.^d—Treat 2 grams of the coffee with 10 cc of water and digest for 36 hours, add 25 cc of 90 per cent alcohol and digest 24 hours more, filter and wash with 90 per cent alcohol. The filtrate contains tannin, caffeine, color, and fat. Heat the filtrate to the boiling point and add a saturated solution of lead acetate. If this is carefully done, a caffetannate of lead will be precipitated containing 49 per cent of lead. As soon as the precipitate has become flocculent, collect on a tared filter, wash with 90 per cent alcohol until free from lead, wash with ether, dry, and weigh. The precipitate has the following composition: $Pb_2(C_{15}H_{11}O_8)_2$. The weight of the precipitate multiplied by 0.51597 gives the weight of the caffetannic acid.

(3) BEER.

It is recommended—

That the changes in methods and the new methods recommended by the referee on beer be printed in the Proceedings and further studied.

Adopted.

These changes in methods are as follows, references being made to Bureau of Chemistry Bulletin No. 65, Provisional Methods for the Analysis of Foods, page 92 et seq.:

5. For "Determination of Original Gravity of Wort," read "Determination of the Percentage of Extract and Specific Gravity of Original Wort."

^a Ibid., p. 26, section (g).

^b Transactions of the Royal Society of Canada, 1887.

^c Archiv. der Pharm., 1885, 827.

^d U. S. Dept. of Agr., Bureau of Chemistry, Bul. 13, Part 7, p. 908.

6. Determination of the Degree of Fermentation;
Calculate from the formula:

$$D = \frac{200a}{B}$$

in which D is the degree of fermentation, *a* the percentage of alcohol, and B the percentage of extract originally contained in the wort from which the beer was produced.

8. Determination of Volatile Acids:

The volatile acid, as acetic acid, is determined by titrating 20 cc of the alcoholic distillate with decinormal sodium hydroxid solution, using phenolphthalein as an indicator. The number of cubic centimeters of decinormal alkali employed multiplied by 0.030 gives the acidity expressed as grams of acetic acid per 100 cc.

13. Determination of Phosphoric Acid:

Measure out 50 cc of the original beer, free from carbonic acid, into a small beaker. Add 5 cc of an acid solution of sodium acetate and heat to boiling. Run in from a burette standard uranium acetate solution, one-half cc at a time, testing each time, until a drop of the beer when placed on a white plate colors a drop of potassium ferrocyanid slightly brown. The number of cubic centimeters of the uranium acetate solution necessary multiplied by 0.01 gives the per cent of phosphoric acid in the beer. If the beer is very dark, employ the official gravimetric or volumetric method, using the residue obtained in the determination of the ash.

(4) DISTILLED LIQUORS.

It is recommended—

1. That the association consider the substitution of the alcohol tables given in the Gaugers' Manual of the Bureau of Internal Revenue, Treasury Department, for the alcohol tables of the association.

Adopted.

2. That the Anthor test for caramel, as modified for distilled liquors by Lasche, be adopted as provisional.

Adopted.

The modification reads as follows:

Add 10 cc of paraldehyde to 5 cc of the sample contained in a test tube and shake. Then add absolute alcohol, a few drops at a time, shaking after each addition until the mixture becomes clear. Allow to stand. Turbidity (after ten minutes) is indication of caramel.—The Brewer Distiller, May, 1903.

3. That the referee make a critical study of the additional methods suggested by collaborating analysts this year for the presence of artificial coloring matter and other tests to distinguish adulterated liquors.

Adopted.

The principal methods suggested are as follows:

(1) *Ether Extract (Gudeman)*: Evaporate on water bath 100 cc of whisky to 25 cc, make up to original bulk and evaporate to 50 cc, make up to original bulk, cool, and take specific gravity. Shake out with 50 cc of ether twice, using a centrifugal machine if the separation is not good. Observe color of ether extract, evaporate to small bulk on the water bath, and to dryness spontaneously. Residue can be weighed after drying over sulphuric acid for from 48 to 72 hours. Observe color of residue, whether resinous and oily, and the bouquet. Straight whiskies aged in wood will be resinous, oily, and have a strong bouquet. Quantity of extract residue not considered of any significance.

(2) *Lead Subacetate Test (Gudeman)*: Use 10 cc of whisky to 1 cc of Subacetate. Observe time of formation and approximate amount of precipitate compared with total volume of solution, manner of settling, and color. Note also the amount of precipitate formed in 10 minutes and the amount formed in 16 hours' standing without agitation of any kind. The precipitate from straight whiskies will be gelatinous and not settle to more than one-fourth of the bulk in 16 hours. Compounded whiskies and mixed whiskies will settle quicker and the precipitate will be firmer: i. e., the amount of precipitate after 16 hours'

standing is an indication of the character of the whisky and gives an approximate idea of the extent of the mixture.

(3) *Chloroform Absorption Test (Lasche)*: If to 5 cc of whisky contained in a test tube 5 cc of chloroform are added and then an addition of 10 cc of water made and shaken carefully once or twice, avoiding an emulsion, the chloroform will absorb the color of the aqueous layer, leaving it colorless (straight whisky). If caramel is the coloring of a whisky the chloroform layer will remain absolutely colorless, while the aqueous layer will remain colored. If caramel was used to reinforce the color of whisky both layers will be colored.

(4) *Qualitative Tests Recommended by Sawyer*:

a. Ferric-alum test for tannin. Three or four drops of a 1 per cent solution added to about 5 cc of each sample.

b. Molisch α -Naphthol test for carbohydrates. See Mulliken, *Identification of Pure Organic Compounds*, page 26.

c. Cobalt nitrate test for sucrose. See Wiley, *Principles and Practice of Agricultural Analysis*, 3: 189. (For 5 cc read "0.5," line 17.)

(5) For the determination of acidity as acetic acid, ethers as ethyl acetate and fusel oil as amyl alcohol, use the excellent method given in the third edition of Allen's *Commercial Organic Analysis*, volume 1, page 154. (McCandless.)

(6) Quantitative determination of fusel oil (isoamyl alcohol) in rectified spirits, by means of salicylic aldehyde. Komorowski, *Chemiker Zeitung*, No. 66, page 807, and No. 88, page 1086, 1903.

4. That the referee make a further study of methods for the estimation of fusel oil.

Adopted.

(5) PRESERVATIVES.

It is recommended—

1. That Method B, page 108, of Bulletin 65,^a for the determination of formaldehyde be discontinued.

Adopted.

(2) That the following methods for determining formaldehyde, etc., be given further trial by the association:

A. ARNOLD AND C. MENTZEL.

Zts. Nahr. Genussm., 1902, 5: 353.

A red color is given by formaldehyde with ferric salts, especially in alcoholic solutions. Mix 5 cc of an alcoholic solution of the substance with 0.03 gram of phenylhydrazin hydrochlorid and 4 drops of ferric chlorid solution; from 10 to 12 cc of concentrated sulphuric acid are then added, keeping the mixture cool. An intense red color is formed. A precipitate is formed which can be dissolved by the addition of either concentrated sulphuric acid, keeping the liquid cool, or by alcohol. With meats and fats the formaldehyde should first be extracted with alcohol and the filtrate tested. Milk is shaken with an equal volume of absolute alcohol and the filtrate employed. In pale beers the coloring matter may be seen without previous treatment, and in dark beers in the froth when the mixture is shaken. In very dark beers it is necessary to add the reagent as directed above and extract with ether, subsequently evaporating the ethereal extract to dryness and treating the residue with alcohol and concentrated sulphuric acid, when the color reappears.

B. RIMINI.

Ann. di Farmacol., 1898, 97: abs. *Chem. Centrbl.*, 1898, pt. 1, p. 1152; abs. *J. Soc. Chem. Ind.*, 1898, 17: 697.

The author gives two extremely sensitive color reactions, which are characteristic for formaldehyde only, and are specially suitable for the detection of the latter in milk. (1) Fifteen cubic centimeters of a very dilute formaldehyde solution are treated with 1 cc of a dilute solution of phenylhydrazin hydrochlorid, then with a few drops of freshly prepared sodium nitroprussid solution.

^a Provisional methods for the analysis of foods, Bureau of Chemistry, Department of Agriculture.

and finally with concentrated caustic soda solution. A blue color is formed, which, after a long time, changes to red. This reaction is capable of indicating formaldehyde in milk, even in a dilution of 1 in 30,000. (2) The second reaction is obtained in a similar manner, except that iron chlorid is used instead of sodium nitroprussid, followed by concentrated hydrochloric acid, instead of caustic soda. This gives a red color, which changes, after some time, to orange yellow.

C. ARNOLD AND C. MENTZEL.

Chem. Zeit., 1902, 26: 246.

Abs. J. Chem. Soc., 1902 (2), 82: 367; abs. Chem. Centrbl., 1902, pt. 1, p. 1077.

The following tests may be applied directly to liquid foods or an aqueous or alcoholic extract of solid foods:

In 3 to 5 cc of the liquid (milk, for instance) is dissolved a lump of phenylhydrazin hydrochlorid the size of a pea, 2 to 4 drops (not more) of a 5 to 10 per cent solution of sodium nitroprussid are added, and finally 8 to 12 drops of 10 to 15 per cent sodium hydroxid. In the presence of even traces of formaldehyde a fairly permanent blue or bluish-green color is produced. The test is rendered still more delicate by substituting potassium ferricyanid for the nitroprussid, but it can not then be recommended for milk or meat preparations containing blood-coloring matter; in case of an alcoholic solution this must be well diluted with water to prevent precipitation of potassium ferricyanid.

Milk is examined directly. Meat is finely comminuted, extracted with 2 volumes of hot water, and the liquid pressed out and employed for the test. Fats (5 to 10 grams) are warmed above the melting point with 10 cc of from 80 to 95 per cent alcohol, thoroughly shaken, cooled, poured through a moistened filter, and the filtrate employed.

D. M. JORISSEN.

Service de Surveillance des Aliments en Belgique; through Bul. Soc. Chim., 1897, 167. Abs. Analyst 1897, 22: 282.

Several drops of a 10 per cent aqueous solution of phloroglucinol are added to about 10 cc of the milk, the mixture shaken, and a few drops of a solution of caustic soda or potash added. A red coloration is produced with milk containing as little as 1 part of formalin in 20,000, whilst normal milk gives no reaction.

Adopted.

(6) THE SEPARATION OF VEGETABLE PROTEIDS.

It is recommended—

I. That for the present no attempt be made, on the results of the following method, to separate the proteids of wheat into individuals and that only such names be applied as describe the process of separation, viz. (a) proteids soluble in alcohol; (b) proteids insoluble in alcohol; (c) proteids soluble in dilute salt solution.

Adopted.

II. That the following method for the separation of the proteids of wheat be used provisionally:

A. *Total Proteids*.—Determine total nitrogen by the Gunning method. Nitrogen $\times 5.68$ = total proteids.

B. *Proteids Soluble in Alcohol*.—1. Weigh out two grams of flour into a small flask holding only slightly more than 100 cc, about 110 cc. Add 100 cc of 70 per cent alcohol and shake thoroughly for fifteen minutes. Allow to stand eighteen hours and filter into a Kjeldahl digestion flask. Wash the residue with 100 cc of alcohol. Add to the total filtrate 5 to 10 cc of concentrated sulphuric acid and distil off the excess alcohol, continuing the distillation until fumes appear. Determine nitrogen by the Gunning method:

$$\text{Nitrogen} \times 5.68 = \text{proteids soluble in water.}$$

2. Determine proteids soluble in alcohol by Snyder's polariscopic method. (J. Amer. Chem. Soc., 2: 263.)

C. *Proteids Insoluble in Alcohol*.—Subtract proteids soluble in alcohol from total proteids to obtain proteids insoluble in alcohol.

D. *Proteids Soluble in Dilute Salt Solution*.—Use a 5 per cent solution of potassium sulphate. Place 4 grams of the flour in a flask such as is used in B 1, and introduce exactly 100 cc of the salt solution. Shake thoroughly and allow to stand, with frequent shakings, for eighteen hours, or, better still, agitate in a shaker for six hours. After standing to settle, filter off 50 cc of the liquid, pouring back the first portions of the filtrate until it filters clear, and determine the nitrogen therein by the Gunning method. The amount multiplied by 2 gives the nitrogen in the original flour. This result multiplied by 5.68 gives the amount of proteids in the flour soluble in a 5 per cent potassium sulphate solution.

Adopted.

III. That further tests as to the overlapping of the different proteids be made.
Adopted.

(7) SEPARATION OF MEAT PROTEIDS.

It is recommended—

That the methods given by the referee for the determination of ammonia, chlorin, and phosphoric acid be adopted as provisional and the method suggested for the determination of xanthin bases be further studied.

Adopted.

The methods referred to are as follows:

EXAMINATION OF MEAT EXTRACTS.

Ammonia.—By the magnesium oxid method, as described in Bulletin 46, page 21.

Acidity.—Titrate with standard alkali solution, using litmus paper as an indicator. The solution may advantageously be removed from the beaker and placed on the litmus paper by means of a capillary tube.

Phosphorus.—The organic matter should be destroyed by one of the methods given in Bulletin 46, page 12, and phosphoric acid determined by either the gravimetric or volumetric molybdate method described in Bulletin 46, pages 12 and 14.

Chlorin.—Determine chlorin by titration with sulphocyanid, according to Volhard. For ordinary purposes the solution of the ash may be employed. More exact results may be obtained by dissolving about 1 gram of the meat extract in 20 cc of a 5 per cent solution of sodium carbonate, evaporating to dryness, and thoroughly igniting. The residue is then extracted with hot water, filtered and washed, after which the filter and contents are returned to a platinum dish and ignited. The contents of the dish are then dissolved in nitric acid, added to the filtrate, and the chlorin content determined as indicated above.

Xanthin Bases (Schittenhelm's Method).—Dissolve from 3 to 5 grams of extract in 100 cc of water, transfer to a 10-inch porcelain dish and add 500 cc of a 1 per cent solution of sulphuric acid. Heat on the water bath for 4 or 5 hours, finally evaporating to a volume of from 75 to 100 cc, neutralize with potassium hydroxid, using litmus paper as an indicator. Transfer to a beaker, add 15 cc of a solution of potassium bisulphate and from 15 to 20 cc of a 15 per cent solution of copper sulphate, cover with a watch glass, and let stand over night. Filter and wash with dilute copper sulphate. Return the precipitate to the original beaker, add sodium sulphid, acidify with acetic acid, and warm on the steam bath. Filter hot and wash with hot water. Treat the filtrate with 10 cc of 10 per cent hydrochloric acid and evaporate it on the steam bath to about 10 cc. Filter and wash, make ammoniacal, and add in slight excess a 3 per cent solution of ammoniacal silver nitrate. Let stand over night, filter, wash out all ammonia carefully, and determine nitrogen in the precipitate. The result is the nitrogen of the xanthin bases.

MOTIONS BEARING ON THE WORK OF COMMITTEES, 1905.

Mr. WHEELER. I move that a committee of five be appointed from this association to define the term "plant food" and that an invitation be extended to the

botanical section of the Association for the Advancement of Science to appoint a similar committee of five to confer with the committee from this association.

Passed.

Mr. VAN SLYKE. Whereas the methods employed by the Association of Official Agricultural Chemists for the analysis of soils and those employed by the Bureau of Soils of the United States Department of Agriculture yield such entirely different results where they should be identical,

Resolved, That a committee be appointed to consider the matter and to consult with the Secretary of Agriculture with a view to bringing about greater harmony in respect to methods employed in soil analysis in the United States and the conclusions based upon such analyses.

L. L. VAN SLYKE,

HARRY SNYDER,

G. S. FRAPS,

Committee on Resolutions.

Carried.

**OFFICERS, REFEREES, AND COMMITTEES OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR 1905.**

President.

Mr. C. L. PENNY, Newark, Del.

Vice-President.

Mr. C. G. HOPKINS, Urbana, Ill.

Secretary.

Mr. H. W. WILEY, Washington, D. C.

Additional members of Executive Committee.

Mr. C. A. BROWNE, Jr., New Orleans, La.

Mr. R. W. THATCHER, Pullman, Wash.

Referees.

Phosphoric acid: E. W. Magruder, Richmond, Va.

Nitrogen:

Determination of nitrogen: F. A. Urner, Geneva, N. Y.

Separation of nitrogenous bodies: R. Harcourt, Guelph, Canada (milk and cheese proteids).

Potash: G. S. Fraps, College Station, Tex.

Soils: C. G. Hopkins, Urbana, Ill.

Dairy products: G. E. Patrick, Washington, D. C.

Foods and feeding stuffs: J. O. LaBach, Lexington, Ky.

Food adulteration: W. D. Bigelow, Washington, D. C.

Sugar: L. S. Munson, Washington, D. C.

Tannin: H. C. Reed, Stamford, Conn.

Insecticides: B. H. Smith, Washington, D. C.

Inorganic plant constituents: R. W. Thatcher, Pullman, Wash.

Medicinal plants and drugs: L. F. Kebler, Washington, D. C.

Associate referees.

Phosphoric acid: J. A. Bizzell, Ithaca, N. Y.

Nitrogen:

Determination of nitrogen: J. H. Gibboney, Blacksburg, Va.

Separation of nitrogenous bodies:

Meat proteids: W. D. Bigelow, Washington, D. C.

Vegetable proteids: J. S. Chamberlain, Washington, D. C.

Potash: A. L. Knisely, Corvallis, Oreg.

Soils: R. H. Loughridge, Berkeley, Cal.

Dairy products: F. W. Woll, Madison, Wis.

Foods and feeding stuffs: J. K. Haywood, Washington, D. C.

Food adulteration:

- (1) Colors: W. G. Berry, Appraiser's Office, New York, N. Y.
- (2) Saccharine products, including confectionary: J. Hortvet, St. Paul, Minn.
- (3) Fruit products: J. S. Burd, Moscow, Idaho.
- (4) Wine: G. E. Colby, Berkeley, Cal.
- (5) Beer: H. E. Barnard, Concord, N. H.
- (6) Distilled liquors: C. A. Crampton, Washington, D. C.
- (7) Vinegar: Richard Fischer, Madison, Wis.
- (8) Flavoring extracts: E. M. Chace, Washington, D. C.
- (9) Spices: A. L. Winton, New Haven, Conn.
- (10) Baking powder and baking chemicals: R. O. Brooks, Trenton, N. J.
- (11) Meat and fish: M. E. Jaffa, Berkeley, Cal.
- (12) Fats and oils: L. M. Tolman, Washington, D. C.
- (13) Dairy products: A. E. Leach, Boston, Mass.
- (14) Cereal products: A. McGill, Ottawa, Canada.
- (15) Infants and invalids' foods: H. W. Wiley, Washington, D. C.
- (16) Vegetables: W. N. Berkeley, San Juan, P. R.
- (17) Condiments other than spices: J. D. Hird, Washington, D. C.
- (18) Cocoa and cocoa products: E. N. Eaton, Chicago, Ill.
- (19) Tea and coffee: H. C. Lythgoe, Boston, Mass.
- (20) Preservatives: W. D. Bigelow, Washington, D. C.

Sugar:

Molasses methods: H. E. Sawyer, Boston, Mass.

Special analytical methods: C. A. Browne, jr., Audubon Park, La.

Tannin: F. P. Veitch, Washington, D. C.

Insecticides: S. Avery, Lincoln, Nebr.

Inorganic plant constituents: F. T. Shutt, Ottawa, Canada.

SPECIAL COMMITTEES.

Food Standards.

Mr. William Frear, State College, Pa., chairman.

Mr. H. W. Wiley, Washington, D. C.

Mr. H. A. Weber, Columbus, Ohio.

Mr. M. A. Scovell, Lexington, Ky.

Mr. E. H. Jenkins, New Haven, Conn.

Fertilizer Legislation.

Mr. H. W. Wiley, Washington, D. C., chairman.

Mr. B. W. Kilgore, Raleigh, N. C.

Mr. H. B. McDonnell, College Park, Md.

Mr. H. A. Huston, St. Louis, Mo.

Mr. B. B. Ross, Auburn, Ala.

Testing Chemical Reagents.

Mr. L. F. Kebler, Washington, D. C., chairman.

Mr. A. L. Winton, New Haven, Conn.

Mr. B. W. Kilgore, Raleigh, N. C.

Unification of Terms for Reporting Analytical Results.

Mr. R. J. Davidson, Blacksburg, Va., chairman.

Mr. C. G. Hopkins, Urbana, Ill.

Mr. W. D. Bigelow, Washington, D. C.

Mr. G. S. Fraps, College Station, Tex.

Mr. C. A. Browne, jr., Audubon Park, New Orleans, La.

Unification of Soil Methods.

Mr. L. L. Van Slyke, Geneva, N. Y., chairman.

Mr. H. J. Wheeler, Kingston, R. I.

Mr. F. K. Cameron, Washington, D. C.

Definition of "Plant Food."

Mr. H. W. Wiley, Washington, D. C., chairman.

Mr. H. J. Wheeler, Kingston, R. I.

Mr. L. L. Van Slyke, Geneva, N. Y.

Mr. E. W. Magruder, Richmond, Va.

Mr. B. W. Kilgore, Raleigh, N. C.

O

